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The attached documents are exact copies of the European patent application described on the following page, as originally filed.

Les documents fixés à cette attestation sont conformes à la version initialement déposée de la demande de brevet européen spécifiée à la page suivante.

Patentanmeldung Nr. Patent application No. Demande de brevet n°

00850135.5

Der Präsident des Europäischen Patentamts;
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets
p.o.

I.L.C. HATTEN-HECKMAN

DEN HAAG, DEN
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Sheet 2 of the certificate
Page 2 de l'attestation

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Process for sizing paper

The present invention relates to a process for sizing paper comprising adding to a suspension containing cellulosic fibres a sizing dispersion comprising a polymer (a), and a sizing promoter comprising a polymer (b), wherein polymer (a) contains at least one aromatic group and polymer (b) contains at least one aromatic group.

Background

Dispersions or emulsions of sizing agents are used in papermaking in order to give paper and paper board improved resistance to wetting and penetration by various liquids. The sizing dispersions are usually added to an aqueous suspension containing cellulosic fibres, optional fillers and various additives. The aqueous suspension is fed into a headbox ejecting the suspension onto a wire where a wet web of paper is formed. To the suspension is further commonly added compounds such as starches and microparticulate materials which facilitate the dewatering of the suspension on the wire. The water drained from the wire, referred to as white water, is usually partly recirculated in the papermaking process. The cellulosic suspension contains a certain amount of non-fibrous material, for example fillers, charged polymers, sizing agents and various charged contaminants, i.e. anionic trash, electrolytes, colloidal substances, etc.. Part of the non-fibrous material has an influence on the sizing efficiency and will likely impair the sizing efficiency. High amounts of charged compounds such as high contents of salts in the suspension renders a suspension which is increasingly difficult to size, i.e. to obtain a paper with satisfactory sizing properties. Other compounds contained in the suspension which deteriorates sizing are various lipophilic wood extractives which may come from recycled fibres and high yield pulps, i.e. mechanical pulps. An increased amount of added sizing agent often improve sizing, however, leading to higher costs as well an increased accumulation of sizing agents in the white water. The accumulation of non-fibrous material as well as any other component present in the suspension will be even more pronounced in mills where white water is extensively recirculated with the introduction of only low amounts of fresh water into the papermaking process. Thus, it is an objective of the present invention to further improve sizing. Another objective of the present invention is to improve sizing when applying sizes on cellulosic suspensions having high conductivities. Yet further objectives will appear hereinafter.

WO 99/55964 refers to a process for production of paper, where a drainage and retention aid is added to a suspension comprising a cationic or amphoteric polysaccharide having a hydrophobic group. The polysaccharide may be used in conjunction with anionic microparticulate materials and sizing agents.

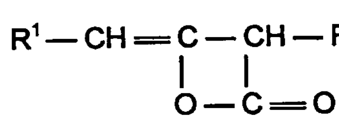
WO 99/55965 relates to a process for production of paper, where a drainage and retention aid is added to a suspension comprising a cationic organic polymer having an

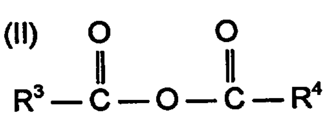
aromatic group. The cationic organic polymer is suitably used together with anionic microparticulate materials.

It has been found that the invention according to the claims surprisingly improves sizing of cellulosic suspensions having high conductivities. More specifically, the invention refers to a process for sizing paper comprising adding to a suspension containing cellulosic fibres a sizing dispersion comprising a polymer (a), and a sizing promoter comprising a polymer (b) and optionally a polymer (c), wherein polymer (a) contains at least one aromatic group, polymer (b) contains at least one aromatic group and polymer (c) contains at least one aromatic group.

Invention

The sizing dispersion added to the suspension comprises a polymer (a) and suitably any sizing agent known, such as non-cellulose-reactive agents including rosins, e.g. fortified and/or esterified rosins, waxes, fatty acids and resin acid derivatives, e.g. fatty amides and fatty esters, e.g. glycerol triesters of natural fatty acids, and/or cellulose-reactive agents. Preferably, the sizing dispersion contains at least one cellulose-reactive sizing agent. The cellulose-reactive sizing agents comprised in the sizing dispersion can be selected from any cellulose-reactive agents known in the art. Suitably, the sizing agent is selected from the group consisting of hydrophobic ketene dimers, ketene multimers, acid anhydrides, organic isocyanates, carbamoyl chlorides and mixtures thereof, preferably ketene dimers and acid anhydrides, most preferably ketene dimers. Suitable ketene dimers have the general formula (I) below, wherein R^1 and R^2 represent saturated or unsaturated hydrocarbon groups, usually saturated hydrocarbons, the hydrocarbon groups suitably having from 8 to 36 carbon atoms, usually being straight or branched chain alkyl groups having 12 to 20 carbon atoms, such as hexadecyl and octadecyl groups. In a preferred embodiment, the ketene dimers are liquid at ambient temperature, i.e. at 25 °C, suitably at 20 °C. Suitable acid anhydrides can be characterized by the general formula (II) below, wherein R^3 and R^4 can be identical or different and represent saturated or unsaturated hydrocarbon groups suitably containing from 8 to 30 carbon atoms, or R^3 and R^4 together with the -C-O-C- moiety can form a 5 to 6 membered ring, optionally being further substituted with hydrocarbon groups containing up to 30 carbon atoms. Examples of acid anhydrides which are used commercially include alkyl and alkenyl succinic anhydrides and particularly isooctadecenyl succinic anhydride.

(I) 

(II) 

Suitable ketene dimers, acid anhydrides and organic isocyanates include the compounds disclosed in U.S. Pat. No. 4,522,686, which is hereby incorporated herein by reference. Examples of suitable carbamoyl chlorides include those disclosed in U.S. Pat. No. 3,887,427 which is also incorporated herein by reference.

According to the present invention a sizing dispersion comprising a polymer (a) containing at least one aromatic group, and a sizing promoter comprising a polymer (b) containing at least one aromatic group and optionally a polymer (c) containing at least one aromatic group are added to a suspension containing cellulosic fibres.

The polymer (a), polymer (b) and polymer (c), preferably include, independently from each other, any of the polymers mentioned below. Polymers (a), (b) and (c) are for simplicity referred to as "the polymer" below. The polymer can be non-ionic or contain charged groups of the same charge or opposite charges. The polymer suitably is anionic, cationic or amphoteric, preferably the polymer has an overall anionic or cationic charge and can be referred to as a polyelectrolyte. Furthermore, the polymer may be derived from natural sources or can be a synthetic polymer. The polymer can be linear, branched or cross-linked, suitably linear or branched. Preferably, the polymer is water-soluble or water-dispersable. The aromatic group of polymer can be present in the polymer backbone or, preferably, the aromatic group can be a pendent group attached to or extending from the polymer backbone or be present in a pendent group that is attached to or extending from the polymer backbone (main-chain). The polymer containing at least one aromatic group is suitably an organic polymer having an overall anionic or cationic charge. (The organic polymers having an overall cationic charge may be derived from natural sources or synthetic polymers.)

The polymer comprised in the sizing dispersion and/or comprised in the sizing promoter according to the present process may be derived from natural sources, i.e. polysaccharides, preferably aromatic substituted cationic or amphoteric polysaccharides, i.e. containing at least one aromatic group and one or more cationic groups, the cationic groups being suitably tertiary or quaternary ammonium groups. The polysaccharides may also contain one or more anionic groups which can be, for example, phosphate, phosphonate, sulphate, sulphonate or carboxylic acid groups and they are preferably phosphate groups. If present, the anionic groups can be native or introduced by means of chemical treatment in conventional manner; native potato starch contains a substantial amount of covalently bound phosphate monoester groups. In amphoteric polysaccharides, cationic groups are preferably present in a predominant amount.

The aromatic group of the polysaccharide can be attached to a heteroatom like oxygen present in the polysaccharide. Preferably, the aromatic group is attached to a heteroatom, e.g. nitrogen or oxygen, the heteroatom optionally being charged, for example

when it is a nitrogen. The aromatic group can also be attached to a group comprising a heteroatom, e.g. amide, ester or ether, which groups can be attached to the polysaccharide backbone (main-chain), for example via a chain of atoms. Example of suitable aromatic groups and groups comprising an aromatic group include aryl and aralkyl groups, e.g. phenyl, phenylene, naphthyl, phenylene, xylylene, benzyl and phenylethyl; nitrogen-containing aromatic (aryl) groups, e.g. pyridinium and quinolinium, as well as derivatives of these groups where one or more substituents attached to said aromatic groups can be selected from hydroxyl, halides, e.g. chloride, nitro, and hydrocarbon groups having from 1 to 4 carbon atoms.

Particularly suitable polysaccharides comprised in the sizing dispersion and/or comprised in the sizing promoter include those comprising the general structural formula (I):

$$P-(-A-\overset{\displaystyle R_1 \,|}{\underset{\displaystyle | \, R_3}{N^+}}-R_2)_n \quad X^- \qquad \text{(I)}$$

wherein P is a residue of a polysaccharide; A is a group attaching N to the polysaccharide residue, suitably a chain of atoms comprising C and H atoms, and optionally O and/or N atoms, usually an alkylene group with from 2 to 18 and suitably 2 to 8 carbon atoms, optionally interrupted or substituted by one or more heteroatoms, e.g. O or N, e.g. an alkyleneoxy group or hydroxy propylene group ($-CH_2-CH(OH)-CH_2-$); R_1 and R_2 are each H or, preferably, a hydrocarbon group, suitably alkyl, having from 1 to 3 carbon atoms, suitably 1 or 2 carbon atoms; R_3 is an aromatic hydrocarbon group including aralkyl groups, e.g. benzyl and phenylethyl groups; n is an integer from about 2 to about 300,000, suitably from 5 to 200,000 and preferably from 6 to 125,000 or, alternatively, R_1, R_2 and R_3 together with N form a aromatic group containing from 5 to 12 carbon atoms; and X^- is an anionic counterion, usually a halide like chloride.

The aromatic group modified cationic or amphoteric polysaccharide can have a degree of substitution varying over a wide range; the degree of cationic substitution (DS_C) can be from 0,01 to 0,5, suitably from 0,02 to 0,3, preferably from 0,025 to 0,2, the degree of aromatic substitution (DS_H) can be from from 0,01 to 0,5, suitably from 0,02 to 0,3, preferably from 0,025 to 0,2, and the degree of anionic substitution (DS_A) can be from 0 to 0,2, suitably from 0 to 0,1, preferably from 0 to 0,05.

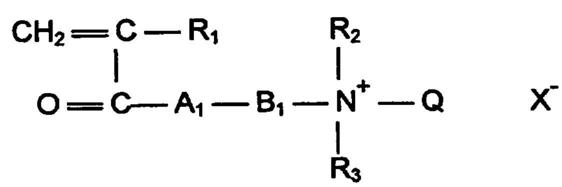
The polysaccharides can be prepared by subjecting a polysaccharide to cationic and aromatic modification in known manner using one or more agents containing a cationic group and/or a aromatic group, for example by reacting the agent with the polysaccharide in the presence of an alkaline substance such as an alkali metal or alkaline earth metal hydroxide. The polysaccharide to be subjected to cationic and aromatic modification can be

non-ionic, anionic, amphoteric or cationic. Suitable modifying agents include non-ionic agents such as, for example, aralkyl halides, e.g. benzyl chloride and benzyl bromide; the reaction products of epichlorohydrin and dialkylamines having at least one substituent comprising an aromatic group as defined above, including 3-dialkylamino-1,2-epoxypropanes; and cationic agents such as, for example, the reaction product of epichlorohydrin and tertiary amines having at least one substituent comprising an aromatic group as defined above, including trialkylamines, alkaryldialkylamines, e.g. dimethylbenzylamine; arylamines, e.g. pyridine and quinoline. Suitable cationic agents of this type include 2,3-epoxypropyl trialkylammonium halides and halohydroxypropyl trialkylammonium halides, e.g. N-(3-chloro-2-hydroxypropyl)-N-(hydrophobic alkyl)-N,N-di(lower alkyl)ammonium chloride and N-glycidyl-N-(hydrophobic alkyl)-N,N-di(lower alkyl)ammonium chloride where the aromatic group is as defined above, notably octyl, decyl and dodecyl, and the lower alkyl is methyl or ethyl; and halohydroxypropyl-N,N-dialkyl-N-alkarylammonium halides and N-glycidyl-N-(alkaryl)-N,N-dialkylammonium chloride, e.g. N-(3-chloro-2-hydroxypropyl)-N-(alkaryl)-N,N-di(lower alkyl)ammonium chloride where the alkaryl and lower alkyl groups are as defined above, particularly N-(3-chloro-2-hydroxypropyl)-N-benzyl-N,N-dimethylammonium chloride; and N-(3-chloro-2-hydroxypropyl) pyridinium chloride. Generally, when using a non-ionic aromatic agent, the polysaccharide is suitably rendered cationic by using any of the cationic agents known in the art before or after the hydrophobic modification. (Examples of suitable cationic and/or aromatic modifying agents, aromatic group modified polysaccharides and methods for their preparation include those described in U.S. Patent Nos. 4,687,519 and 5,463,127; International Patent Application WO 94/24169, European Patent Application No. 189 935; and S.P. Patel, R.G. Patel and V.S. Patel, Starch/Stärke, 41(1989), No. 5, pp. 192-196, the teachings of which are hereby incorporated herein by reference.).

The polymer, i.e. polymer (a) or polymer (b) or polymer (c), may also be a synthetic polymer suitably an organic synthetic polymer having an overall cationic charge containing at least one aromatic group. The synthetic polymer can be linear, branched or crosslinked, suitably linear or branched. The aromatic group of the synthetic polymer can be present in the polymer backbone or, preferably, it can be a pendent group attached to or extending from the polymer backbone or be present in a pendent group that is attached to or extending from the polymer backbone (main chain). Suitable aromatic (aryl) groups include those comprising a phenyl group, optionally substituted, a phenylene group, optionally substituted, and a naphthyl group, optionally substituted, for example groups having the general formulae $-C_6H_5$, $-C_6H_4-$, $-C_6H_3-$, and $-C_6H_2-$, e.g. in the form of phenylene ($-C_6H_4-$), xylylene ($-CH_2-C_6H_4-CH_2-$), phenyl ($-C_6H_5$), benzyl ($-CH_2-C_6H_5$), phenethyl ($-CH_2CH_2-C_6H_5$), and substituted phenyl (for example $-C_6H_4-Y$, $-C_6H_3Y_2$, and $-C_6H_2Y_3$)

where one or more substituents (Y) attached to the phenyl ring can be selected from hydroxyl, halides, e.g. chloride, nitro, and hydrocarbon groups having from 1 to 4 carbon atoms.

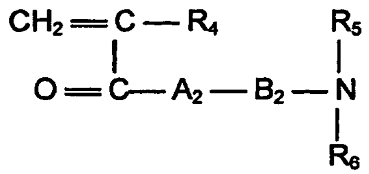
The synthetic polymer can be selected from homopolymers and copolymers prepared from one or more monomers comprising at least one monomer having an aromatic group, suitably an ethylenically unsaturated monomer, and the synthetic polymer is suitably a vinyl addition polymer. The term "vinyl addition polymer", as used herein, refers to a polymer prepared by addition polymerisation of one or more vinyl monomers or ethylenically unsaturated monomers which include, for example, acrylamide-based and acrylate-based monomers. Suitable synthetic polymers include cationic vinyl addition polymers obtained by polymerising a cationic monomer or a monomer mixture comprising a cationic monomer represented by the general formula (II):



(II)

wherein R_1 is H or CH_3; R_2 and R_3 are each or, preferably, an alkyl group having from 1 to 3 carbon atoms, usually 1 to 2 carbon atoms; A_1 is O or NH; B_1 is an alkylene group having from 2 to 8 carbon atoms, suitably from 2 to 4 carbon atoms, or a hydroxy propylene group; Q is a substituent containing an aromatic group, suitably a phenyl or substituted phenyl group, which can be attached to the nitrogen by means of an alkylene group usually having from 1 to 3 carbon atoms, suitably 1 to 2 carbon atoms, and preferably Q is a benzyl group ($-CH_2-C_6H_5$); and X^- is an anionic counterion, usually a halide like chloride. Examples of suitable monomers represented by the general formula (II) include quaternary monomers obtained by treating dialkylaminoalkyl (meth)acrylates, e.g. dimethylaminoethyl (meth)-acrylate, diethylaminoethyl (meth)acrylate and dimethylaminohydroxypropyl (meth)acrylate, and dialkylaminoalkyl (meth)acrylamides, e.g. dimethylaminoethyl (meth)acrylamide, diethyl-aminoethyl (meth)acrylamide, dimethylaminopropyl (meth)acrylamide, and diethylamino-propyl (meth)acrylamide, with benzyl chloride. Preferred cationic monomers of the general formula (II) include dimethylaminoethylacrylate benzyl chloride quaternary salt and dimethylaminoethylmethacrylate benzyl chloride quaternary salt.

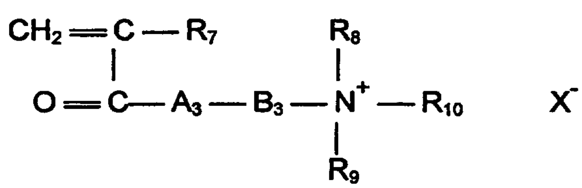
The cationic organic synthetic polymer can be a homopolymer prepared from a cationic monomer having an aromatic group or a copolymer prepared from a monomer mixture comprising a cationic monomer having an aromatic group and one or more copolymerizable monomers. Suitable copolymerizable non-ionic monomers include monomers represented by the general formula (III):



(III)

wherein R_4 is H or CH_3; R_5 and R_6 are each H or a hydrocarbon group, suitably alkyl, having from 1 to 6, suitably from 1 to 4 and usually from 1 to 2 carbon atoms; A_2 is O or NH; B_2 is an alkylene group of from 2 to 8 carbon atoms, suitably from 2 to 4 carbon atoms, or a hydroxy propylene group or, alternatively, A and B are both nothing whereby there is a single bond between C and N (O=C — NR_5R_6). Examples of suitable copolymerizable monomers of this type include (meth)acrylamide; acrylamide-based monomers like N-alkyl (meth)acrylamides and N,N-dialkyl (meth)acrylamides, e.g. N-n-propylacrylamide, N-isopropyl (meth)acrylamide, N-n-butyl (meth)acrylamide, N-isobutyl (meth)acrylamide and N-t-butyl (meth)acrylamide; and dialkylaminoalkyl (meth)acrylamides, e.g. dimethylaminoethyl (meth)acrylamide, diethylaminoethyl (meth)acrylamide, dimethylaminopropyl (meth)acrylamide and diethylaminopropyl (meth)acrylamide; acrylate-based monomers like dialkylaminoalkyl (meth)acrylates, e.g. dimethylaminoethyl (meth)acrylate, diethylaminoethyl (meth)acrylate, t-butylaminoethyl (meth)acrylate and dimethylaminohydroxypropyl acrylate; and vinylamides, e.g. N-vinylformamide and N-vinylacetamide. Preferred copolymerizable non-ionic monomers include acrylamide and methacrylamide, i.e. (meth)acrylamide, and the main polymer is preferably an acrylamide-based polymer.

Suitable copolymerizable cationic monomers include the monomers represented by the general formula (IV):



(IV)

wherein R_7 is H or CH_3; R_8, R_9 and R_{10} are each H or, preferably, a hydrocarbon group, suitably alkyl, having from 1 to 3 carbon atoms, usually 1 to 2 carbon atoms; A_3 is O or NH; B_3 is an alkylene group of from 2 to 4 carbon atoms, suitably from 2 to 4 carbon atoms, or a hydroxy propylene group, and X^- is an anionic counterion, usually methylsulphate or a halide like chloride. Examples of suitable cationic copolymerizable monomers include acid addition salts and quaternary ammonium salts of the dialkylaminoalkyl (meth)acrylates and dialkylaminoalkyl (meth)acrylamides mentioned above, usually prepared using acids like HCl, H_2SO_4, etc., or quaternizing agents like methyl chloride, dimethyl sulphate, etc.; and diallyldimethylammonium chloride. Preferred copolymerizable cationic monomers include

dimethylaminoethyl (meth)acrylate methyl chloride quaternary salt and diallyldimethylammonium chloride. Copolymerizable anionic monomers like acrylic acid, methacrylic acid, various sulfonated vinyl addition monomers, etc. can also be employed and, preferably, in minor amounts.

The synthetic polymer can be prepared from a monomer mixture generally comprising from 1 to 99 mole%, suitably from 2 to 50 mole% and preferably from 5 to 20 mole% of cationic monomer having an aromatic group, preferably represented by the general formula (II), and from 99 to 1 mole%, suitably from 98 to 50 mole%, and preferably from 95 to 80 mole% of other copolymerizable monomers which preferably comprises acrylamide or methacrylamide ((meth)acrylamide), the monomer mixture suitably comprising from 98 to 50 mole% and preferably from 95 to 80 mole% of (meth)acrylamide, the sum of percentages being 100.

The synthetic polymer can also be selected from polymers prepared by condensation reaction of one or more monomers containing an aromatic group. Examples of such monomers include toluene diisocyanates, bisphenol A, phthalic acid, phthalic anhydride, etc., which can be used in the preparation of cationic polyurethanes, cationic polyamideamines, etc.

Alternatively, or additionally, the synthetic polymer can be a polymer subjected to aromatic modification using an agent containing an aromatic group. Suitable modifying agents of this type include benzyl chloride, benzyl bromide, N-(3-chloro-2-hydroxypropyl)-N-benzyl-N,N-dimethylammonium chloride, and N-(3-chloro-2-hydroxypropyl) pyridinium chloride. Suitable polymers for such an aromatic modification include vinyl addition polymers. If the polymer contains a tertiary nitrogen which can be quaternized by the modifying agent, the use of such agents usually results in that the polymer is rendered cationic. Alternatively, the polymer to be subjected to aromatic modification can be cationic, for example a cationic vinyl addition polymer.

Usually the charge density of the synthetic polymer is within the range of from 0.1 to 6.0 meqv/g of dry polymer, suitably from 0.2 to 4.0 and preferably from 0.5 to 3.0.
The weight average molecular weight of synthetic polymers is usually at least about 500,000, suitably above about 1,000,000 and preferably above about 2,000,000. The upper limit is not critical; it can be about 50,000,000, usually 30,000,000 and suitably 25,000,000.

The synthetic polymer of this invention may be in any state such as, for example, in solid form, e.g. powders, in liquid form, e.g. solutions, emulsions, dispersions, including salt dispersions, etc. Examples of suitable synthetic polymers for use in this invention include those described in U.S. Patent Nos. 5,169,540; 5,708,071; and European Patent Applications 183,466; 525,751 and 805,234; the disclosures of which are hereby incorpo-

rated herein by reference. When being added to the stock, the synthetic polymer is suitably in liquid form, e.g. in the form of an aqueous solution or dispersion.

Polymer (a), polymer (b) and polymer (c) can also include, independently from each other, anionic polymers containing at least one aromatic group. The anionic polymer, i.e. having an overall anionic charge, is suitably an organic polymer which may be water-soluble or water-dispersable. The anionic polymer can be linear or branched. Suitably, the aromatic group of the anionic polymer can be present in the polymer backbone or, preferably, it can be a pendant group attached to or extending from the polymer backbone or be present in a pendant group that is attached to or extending from the polymer backbone (main chain). The anionic polymer has suitably at least one aromatic group and at least one anionic group such as a sulphonate, phosphate, phosphonate, sulphate or carboxylic acid group. The anionic group may be directly attached to the aromatic group or can be attached to a chain of atoms which in turn is attached to the aromatic group. Suitable anionic polymers include condensated naphthalene sulphonates, polystyrene sulphonates and lignosulphonate.

The process according to the present invention comprises adding to a suspension containing cellulosic fibres a sizing dispersion comprising a polymer (a) containing at least one aromatic group.

The sizing dispersion can be anionic or cationic charged, i.e. the dispersing and/or stabilising agents present have an overall anionic or cationic charge, respectively. Suitably, the sizing dispersion also contains additional dispersing agents and/or stabilising agents.

Polymer (a) containing at least one aromatic group may be present in the dispersion in amount varying within wide limits depending on, inter alia, the molecular weight of polymer (a), ionic substitution of polymer (a), desired overall charge of the dispersion and sizing agent(s) used. Polymer (a) may be present in the dispersion in an amount of up to 40% by weight, suitably from 0.1 up to 35% by weight and preferably from 0.3 up to 30% by weight based on the sizing agent.

The aqueous sizing dispersion added to the suspension suitably can have a sizing agent content from 0.1 to 50 % by weight based on total dispersion, suitably over 20% by weight. Dispersions comprising ketene dimer sizing agents may have ketene dimer contents from 5 up to 50 % by weight based on total dispersion, preferably from 10 up to 35% by weight. Dispersions, or emulsions, comprising acid anhydride sizing agents may have acid anhydride contents from 0.1 up to 30 % by weight based on total dispersion/emulsion, suitably from 1 up to 20 % by weight. Dispersions containing non-cellulose reactive sizing agents suitably have sizing agent contents from 5 up to 50 % by weight, preferably from 10 up to 35 % by weight.

The amount of sizing agent added to the suspension containing cellulosic fibres can be from 0.01 to 5 % by weight, suitably from 0.05 to 1.0 % by weight, based on dry weight of cellulosic fibres and optional fillers, where the dosage is dependent on the quality of the pulp or paper to be sized, the sizing agent and the level of sizing.

The process for sizing paper according to the present invention comprises adding to a suspension containing cellulosic fibres a sizing dispersion comprising a polymer (a) and a sizing promoter comprising a polymer (b) containing at least one aromatic group. The polymer (b) suitably includes any of the polymers mentions above such as cationic or amphoteric polysaccharides, synthetic polymers or anionic organic synthetic polymers. If polymer (b) is the only polymer containing at least one aromatic group comprised in the sizing promoter, polymer (b) is suitably any of the anionic polymers indicated above, for example lignosulphonates, condensated naphthalene sulphonates and/or polystyrene sulphonates or mixtures thereof. Preferably, polymer (b) forms part of a drainage and retention system comprising two or more components. If polymer (b) is a cationic or amphoteric polymer, i.e. has an overall cationic charge, the sizing promoter suitably further contains anionic microparticulate materials, e.g. anionic organic particles, anionic inorganic particles and water-soluble anionic vinyl addition polymers.

According to one preferred embodiment of the present invention a sizing dispersion having an overall cationic charge comprising a polymer (a) and a sizing promoter comprising a polymer (b) is added to the suspension.

According to another embodiment of the present invention a sizing dispersion having an overall anionic charge comprising a polymer (a) and a sizing promoter comprising a polymer (b) is added to the suspension.

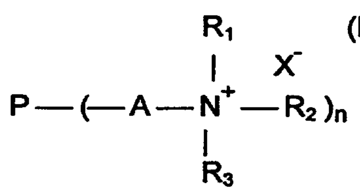
One preferred embodiment of the present invention comprises adding to a suspension containing cellulosic fibres a sizing dispersion comprising a polymer (a) and a sizing promoter comprising a polymer (b) and a polymer (c), wherein polymers (a), (b) and (c) contains at least one aromatic group each. The polymers (a), (b) and (c) can be, independently from each other, any of the polymers mentioned above. Preferably, the sizing promoter comprising a polymer (b) and a polymer (c) can be referred to as a drainage and retention system. The sizing promoter may further comprise components such as anionic microparticulate materials, e.g. anionic organic particles and anionic inorganic particles, water-soluble anionic vinyl addition polymers, low molecular weight cationic organic polymers, aluminium compounds, and combinations thereof.

According to yet another preferred embodiment of the present invention a sizing dispersion comprising a polymer (a) having at least one aromatic group and a sizing promoter comprising a polymer (b) and a polymer (c) both having at least one aromatic group are added to a suspension containing cellulosic fibres, whereby the overall charges of

polymers (b) and (c) are opposite, preferably, polymer (b) has an overall cationic charge, i.e. is cationic and/or amphoteric and polymer (c) has an overall anionic charge, i.e. is anionic and/or amphoteric.

According to yet another preferred embodiment of the present invention a process for sizing paper is provided comprising adding to a suspension containing cellulosic fibres a sizing dispersion comprising a polymer (a), and a sizing promoter comprising a polymer (b) being selected from organic polymers having an overall cationic charge, i.e. a cationic and/or amphoteric organic polymers, specifically a cationic or amphotheric polysaccharide containing at least one aromatic group and/or cationic vinyl addition polymer containing at least one aromatic group; and a polymer (c) being selected from organic polymers having an overall anionic charge, i.e. anionic and/or amphoteric organic polymers including condensated naphthalene sulphonates, polystyrene sulphonates and/or lignosulphonate, or mixtures thereof.

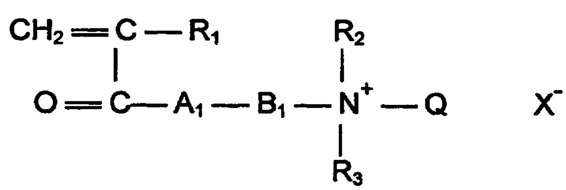
A further preferred embodiment of the present invention is a process for sizing paper comprising adding to a suspension containing cellulosic fibres a sizing dispersion comprising a polymer (a) including any of the polymers mentioned above, i.e. referred to as polymer (a) and/or polymer (b) and/or polymer (c); and a sizing promoter comprising a polymer (b) and a polymer (c), whereby polymer (b) is selected from cationic or amphoteric polysaccharides having the structural formula (I):



(I)

wherein P is a residue of a polysaccharide; A is a chain of atoms comprising C and H atoms attaching N to the polysaccharide residue, R_1 and R_2 are each H or a hydrocarbon group, R_3 is an aromatic hydrocarbon group, n is an integer from 2 up to 300000, and X^- is an anionic counter ion; and

vinyl addition polymers obtained by polymerising a cationic monomer or a monomer mixture comprising a cationic monomer represented by the general formula (II):



(II)

wherein R_1 is H or CH_3; R_2 and R_3 are each an alkyl group having from 1 to 3 carbon atoms, A_1 is O or NH, B_1 is an alkylene group having from 2 to 8 carbon atoms or a hydroxy propylene group, Q is a substituent containing an aromatic group, and X^- is an anionic

counterion; and polymer (c) is selected from condensated naphthalene sulphonate, polystyrene sulphonate and lignosulphonate.

According to yet another preferred embodiment of the present invention a process for sizing paper is provided comprising adding to a suspension containing cellulosic fibres a sizing dispersion comprising a polymer (a) including any of the polymers mentioned above, and a sizing promoter comprising a polymer (b) being selected from cationic and/or amphoteric polysaccharides and a polymer (c) including anionic organic polymers, preferably, lignosulphonates, condensated naphtalene sulphonates and polystyrene sulphonates.

Polymer (b) and optionally polymer (c), or any other components comprised in the sizing promoter may be added separately to the suspension or together/simultaneously to the suspension at essentially the same position in the paper making system. Suitably, polymer (b) or optionally polymer (c) or any other component comprised in the sizing promoter having an overall cationic charge (cationic/amphoteric) is added to the suspension prior to polymer (b) or polymer (c) or any other component having an overall anionic charge. It is further preferred to add polymer (b) or optionally polymer (c) or any other component having an overall cationic charge before a shear stage, which can be selected from pumping, mixing cleaning, etc., and to add polymer (b) or polymer (c) or any other component having an overall anionic charge after the shear stage.

Polymer (b) and (c) may be in any state of aggregation, e.g. in solid form (powder), in liquid form such as solution, emulsion, dispersion, including salt dispersions. When polymer (b) and optionally polymer (c), forming the sizing promoter, are added to the stock, they are preferably provided in liquid form, e.g. in the form of an aqueous solution or dispersion.

The sizing dispersion comprising polymer (a), and the sizing promoter comprising a polymer (b) and suitably a polymer (c) can be added simultaneously or separately to the cellulosic stock, preferably separately, whereby the polymer (b) and/or (c) or any other component comprised in the sizing promoter and the sizing dispersion may be added in any order to the suspension. Preferably, the sizing dispersion is added subsequent to the addition of the promoter, i.e. subsequent both polymer (b) and optionally polymer (c).

Polymer (b) and/or optionally polymer (c) can be added to the stock in amounts which can vary within wide limits depending on, inter alia, type of furnish, filler content, type of filler, point of addition, salt content, etc. Generally, the sizing promoter, i.e. polymer (b) and/or (c) and/or any other component are added in an amount that give the paper improved sizing properties than is obtained when not adding the sizing promoter. Suitably, polymer (b) or polymer (c) are added to the furnish in an amount of at least 0.001 % by weight up to 10 % based on dry furnish substance. If polymer (b) or polymer (c) are polysaccharides, the

polymer is added to the stock in an amount of at least 0.01 %, suitably at least 0.1 % by weight based on dry stock substance, and the upper limit is usually 10 % preferably 2 %. In case polymer (b) or polymer (c) are synthetic cationic polymers they are added to the stock in an amount of at least 0.001 %, suitably at least 0.005 % by weight, based on dry stock substance, whereas the upper limit is usually 3 %, preferably 1.5 % by weight.

The process of the invention is preferably used in the manufacture of paper from a suspension containing cellulosic fibers, and optional fillers, having a high conductivity. Usually, the conductivity of the stock is at least 0.2 mS/cm, suitably at least 0.5 mS/cm, preferably at least 3.5 mS/cm. Very good sizing results have been observed at conductivity levels above 5.0 mS/cm and even above 7.5 mS/cm. Conductivity can be measured by standard equipment such as, for example a WTW LF 539 instrument supplied by Christian Berner. The values referred to above are suitably determined by measuring the conductivity of the cellulosic suspension that is fed into or present in the headbox of the paper machine or, alternatively, by measuring the conductivity of white water obtained by dewatering the suspension. High conductivity levels mean high contents of salts (electrolytes), where the various salts can be based on mono-, di- and multivalent cations like alkali metals, e.g. Na^+ and K^+, alkaline earths, e.g. Ca^{2+} and Mg^{2+}, aluminium ions, e.g. Al^{3+}, $Al(OH)^{2+}$ and polyaluminium ions, and mono-, di- and multivalent anions like halides, e.g., Cl^-, sulfates, e.g. SO_4^{2-} and HSO_4^-, carbonates, e.g. CO_3^{2-} and HCO_3^-, silicates and lower organic acids. The invention is particularly useful in the manufacture of paper from stocks having high contents of salts of di- and multivalent cations, and usually the cation content is at least 200 ppm, suitably at least 300 ppm and preferably at least 400 ppm. The salts can be derived from the cellulosic fibres and fillers used to form the stock, in particular in integrated mills where a concentrated aqueous fibre suspension from the pulp mill normally is mixed with water to form a dilute suspension suitable for paper manufacture in the paper mill. The salt may also be derived from various additives introduced into the stock, from the fresh water supplied to the process, or be added deliberately, etc. Further, the content of salts is usually higher in processes where white water is extensively recirculated, which may lead to considerable accumulation of salts in the water circulating in the process.

The present invention further encompasses papermaking processes where white water is extensively recirculated (recycled), i.e. with a high degree of white water closure, for example where from 0 to 30 tons of fresh water are used per ton of dry paper produced, usually less than 20, suitably less than 15, preferably less than 10 and notably less than 5 tons of fresh water per ton of paper. Recirculation of white water obtained in the process suitably comprises mixing the white water with cellulosic fibres and/or optional fillers to form a suspension to be sized; preferably it comprises mixing the white water with a suspension

containing cellulosic fibres, and optional fillers, before the suspension enters the forming wire for sizing.

Further additives which are conventional in papermaking can of course be used in combination with the additives according to the invention, such as, for example, additional dry strength agents, wet strength agents. The cellulosic suspension, or stock, can also contain mineral fillers of conventional types such as, for example, kaolin, china clay, titanium dioxide, gypsum, talc and natural and synthetic calcium carbonates such as chalk, ground marble and precipitated calcium carbonate.

The process of this invention is used for the production of paper. The term "paper", as used herein, of course include not only paper and the production thereof, but also other sheet or web-like products, such as for example board and paperboard, and the production thereof. The process can be used in the production of paper from different types of suspensions of cellulose-containing fibres and the suspensions should suitably contain at least 25% by weight and preferably at least 50% by weight of such fibres, based on dry substance. The suspensions can be based on fibres from chemical pulp such as sulphate, sulphite and organosolv pulps, mechanical pulp such as thermomechanical pulp, chemo-thermomechanical pulp, refiner pulp and groundwood pulp, from both hardwood and softwood, and can also be based on recycled fibres, optionally from de-inked pulps, and mixtures thereof. The invention is particularly useful in the manufacture of paper from suspensions based on pulps comprising recycled fibres and de-inked pulp, and the content of cellulosic fibres of such origin can be up to 100%, suitably from 20 to 100%.

The invention is further illustrated in the following Examples which, however, are not intended to limit the same. Parts and % relate to parts by weight and % by weight, respectively, unless otherwise stated.

Example 1

The sizing performance of the process was evaluated by using the cobb 60 test.

An anionic sizing dispersion was prepared containing alkyl ketene dimer, condensed naphtalene sulphonate and di(hydrogenated tallow) dimethylammonium chloride. The sizing dispersion had an AKD content of 30% and contained 4% of di(hydrogenated tallow) dimethylammonium chloide and 6% of condensed naphtalene sulphonate, based on AKD. The sizing dispersion was added to the stock in an amount of 5 kg AKD/ tonne dry stock.

A cationic starch with a cationic substitution DS of 0.065 regarding nitrogen containing benzyl groups and/or condensated naphtalene sulphonate (available under the trade name Tamol ®) comprised in the sizing promoter was further added to the furnish. Moreover, additional components comprised in the sizing promoter were added to the

stock where appropriate and indicated by table 1, including cationic starch without aromatic groups with a DS of 0.065 and anionic inorganic silica particles provided as a sol.

The furnish used was based on 80 % by weight of bleached birch/pine (60/40) sulphate pulp and 20 % by weight of $CaCO_3$ refined to 200 CSF and containing 0.3 g/litre stock Na_2SO_4, having a conductivity of 461 μS/cm and a pH of 8,1.

Table 1

	anionic sizing dispersion/ [kg sizing agent/tonne dry stock]	cationic starch containing aromatic groups/[kg /tonne dry stock]	cationic starch (without aromatic groups)/[kg starch/tonne dry stock]
test 1 (ref.)	0,5	0	10
test 2	0,5	10	0
test 3	0,5	10	0

	cond. naphtalene sulphonate / [kg cond./tonne dry stock]	anionic silica particles/[kg silica part./tonne dry stock]	cobb 60/[g/m^2]
test 1(ref.)	0	1	45,2
test 2	0	1	33,5
test 3	1	0	29,3

Example 2

The sizing performance of the process was evaluated (cobb 60 test) using the same anionic sizing dispersion and the same sizing promoters as in example 1, however, calcium chloride was added to the stock to adjust the conductivity to 5000 μS/cm.

Table 2

	anionic sizing dispersion/ [kg sizing agent/tonne dry stock]	cationic starch containing aromatic groups/[kg /tonne dry stock]	cationic starch (without aromatic groups)/[kg starch/tonne dry stock]
test 1 (ref.)	0,5	0	12
test 2	0,5	12	0
test 3	0,5	10	0

	cond. naphtalene sulphonate/ [kg cond./tonne dry stock]	anionic silica particles/[kg silica part./tonne dry stock]	cobb 60/[g/m^2]
test 1(ref.)	0	1,0	75
test 2	0	1,0	28
test 3	1	0	27,8

Example 3

The sizing performance was evaluated using a cationic sizing dispersion which contained 15 % of alkyl ketene dimer, 2 % of cationic starch, and 0.6 % of sodium lignosulphonte based on AKD. The components and added amounts of components comprised in the sizing promoter, apparent from table 3, included condensated naphthalene sulphonate, cationic starch without aromatic groups having a DS of 0.065, cationic starch containing aromatic groups having a DS of 0.065 and anionic inorganic silica particles provided as a sol. The stock used was that of example 2 having a pH of 8.1 and a conductivity of 5000 µS/cm by the addition of calcium chloride to the stock.

Table 3

	cationic sizing dispersion/ [kg sizing agent/tonne dry stock]	cationic starch containing aromatic groups/[kg /tonne dry stock]	cationic starch (without aromatic groups)/[kg starch/tonne dry stock]
test 1 (ref.)	0,5	0	10
test 2	0,5	0	10
test 3	0,5	10	0

	cond. naphtalene sulphonate/ [kg cond./tonne dry stock]	anionic silica particles/[kg silica part./tonne dry stock]	cobb 60/[g/m^2]
test 1 (ref.)	0	1	55
test 2	1	0	34
test 3	1	0	27,8

Claims

1. Process for sizing paper comprising adding to a suspension containing cellulosic fibres a sizing dispersion comprising a polymer (a), and a sizing promoter comprising a polymer (b) c h a r a c t e r i s e d in that polymer (a) contains at least one aromatic group and polymer (b) contains at least one aromatic group.

2. Process for sizing paper comprising adding to a suspension containing cellulosic fibres a sizing dispersion comprising a polymer (a), and a sizing promoter comprising a polymer (b) and a polymer (c), c h a r a c t e r i s e d in that polymer (a) contains at least one aromatic group, polymer (b) contains at least one aromatic group, and polymer (c) contains at least one aromatic group.

3. Process according any of the preceding claims, c h a r a c t e r i s e d in that the sizing dispersion is anionic or cationic.

4. Process according to claim 2, c h a r a c t e r i s e d in that the overall charge of polymer (b) and polymer (c) are opposite.

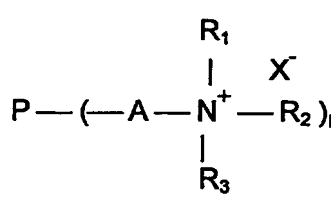
5. Process according to any of the preceding claims, c h a r a c t e r i s e d in that the sizing dispersion and the sizing promoter are added separately to the suspension.

6. Process according to any of the preceding claims, c h a r a c t e r i s e d in that the sizing dispersion comprises a cellulose-reactive sizing agent.

7 Process according to any of the preceding claims, c h a r a c t e r i s e d in that polymer (b) is selected from cationic or amphoteric polysaccharides and cationic vinyl addition polymers and optionally polymer (c) is selected from anionic organic polymers.

8. Process according to claim 7, c h a r a c t e r i s e d in that polymer (c) is selected from condensated naphthalene sulphonate, polystyrene sulphonate and lignosulphonate.

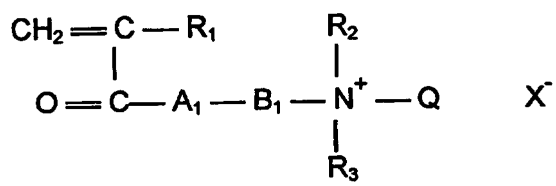
9. Process according to any of the preceding claims, c h a r a c t e r i s e d in that polymer (b) is selected from cationic or amphoteric polysaccharides having the structural formula (I):



(I)

wherein P is a residue of a polysaccharide; A is a chain of atoms comprising C and H atoms attaching N to the polysaccharide residue, R_1 and R_2 are each H or a hydrocarbon group, R_3 is an aromatic hydrocarbon group, n is an integer from 2 up to 300000, and X^- is an anionic counter ion; and

vinyl addition polymers obtained by polymerising a cationic monomer or a monomer mixture comprising a cationic monomer represented by the general formula (II):



(II)

wherein R_1 is H or CH_3; R_2 and R_3 are each an alkyl group having from 1 to 3 carbon atoms, A_1 is O or NH, B_1 is an alkylene group having from 2 to 8 carbon atoms or a hydroxy propylene group, Q is a substituent containing an aromatic group, and X^- is an anionic counterion; and optionally polymer (c) is selected from condensated naphthalene sulphonate, polystyrene sulphonate and lignosulphonate.

10. Process according to any of the preceding claims characterised in that the conductivity of the suspension is at least 3.5 mS/cm.

Abstract

The present invention refers to a process for sizing paper comprising adding to a suspension containing cellulosic fibres a sizing dispersion comprising a polymer (a), and a sizing promoter comprising a polymer (b) and optionally a polymer (c), wherein polymer (a) contains at least one aromatic group, polymer (b) contains at least one aromatic group and polymer (c) contains at least one aromatic group.